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DEFORMATION RESISTANCE OF GLASS CERAMIC MATERIAL

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The production specifics of glass ceramic materials in the $CaO - Al_2O_3 - SiO_2$ system using the continuous rolling and the compression methods are considered. The results of studying the effect of various factors on the value of vertical deformation arising in heat treatment of such materials are described. It is demonstrated that different types of crystallization processes in heat treatment can become the reasons for different deformation resistance levels. An optimum regime for heat treatment of glass ceramic materials produced by continuous rolling is proposed.

One of the topical problems in the production of construction materials is the need to improve the decorative properties and to expand the product range of finishing construction materials in order to meet contemporary requirements. At the same time, artificial materials should not rank below natural materials in properties and exterior appearance.

Glass ceramics occupy an important place among finishing building materials, due to their combination of good decorative and service properties. The production of such materials is a satisfactory solution of the above problem.

The best known glass ceramic material developed in Russia is slag glass ceramic. It consists of fine crystals (0.2 – 1.0 μm) and a residual vitreous phase. The mass content of the crystalline phase in a slag glass ceramic is 50 – 70% [1 – 3]. The glass compositions which serve as the basis for the synthesis of slag glass ceramics belong to the $CaO - Al_2O_3 - SiO_2$ system. The initial materials for producing slag glass ceramics are industrial wastes with additives of quartz sand and small quantities of other components. A continuous rolling method was developed for the production of slag glass ceramics, which significantly decreased the production cost. The valuable physicochemical properties make it possible to use slag glass ceramics in facing of buildings, engineering structures, etc. A drawback of slag glass ceramics consists in the limited color range: only gray and white bulk-tinted tiles used to be manufactured.

Another glass ceramic material developed in Russia is named "sygran" (synthetic garnet) [1, 2]. Similar to slag glass ceramics, Sygran is synthesized on the basis of glasses of the $CaO - Al_2O_3 - SiO_2$ system. Sygran consists of spheroid crystal aggregates up to 5 mm in diameter (spherulites) whose weight content reaches 40 – 50% and the residual vitreous phase between the spherulites. The crystalline phase ensures the high physicomechanical parameters of the material and its attractive exterior appearance, which resembles natural stones, such as garnet or marble. Sygran used to be produced by compression at several Russian glass factories in the form of plates 300 × 300 × 20 mm. However there is a demand for Sygran plates of larger sizes.

The implementation of the continuous rolling method in production of Sygran will make it possible to increase the efficiency, lower the production cost, and expand the range of products.

The production of glass ceramic materials is carried out by the following technological scheme: batch preparation → glass melting → molding of articles → crystallization and annealing of articles. Crystallization in the production of glass ceramics is a technological stage which differs from the technology of traditional glass articles. At this stage, catalyzed crystallization processes occur in glass under heat treatment in the crystallizing furnace, as the result of which a glass ceramic material is formed. As a rule, the heat treatment is implemented in two stages. Crystallization centers are formed in the first stage, and the growth of crystal occurs in the second stage.

The heat treatment of glass ceramics produced by continuous rolling is implemented on a roller conveyor and not on a solid base, as in the case of molding. The crystallization of a glass band on a roller conveyor involves the risk of its vertical deformation, which can lead to a significant deflection of the band between the rollers. In the case of heat treatment on a solid base, such risk is nonexistent. Therefore, one of the main criteria of the suitability of glass for the continuous rolling production method is the absence of significant deformation of the glass band in the course of its crystallization on a roller conveyor.

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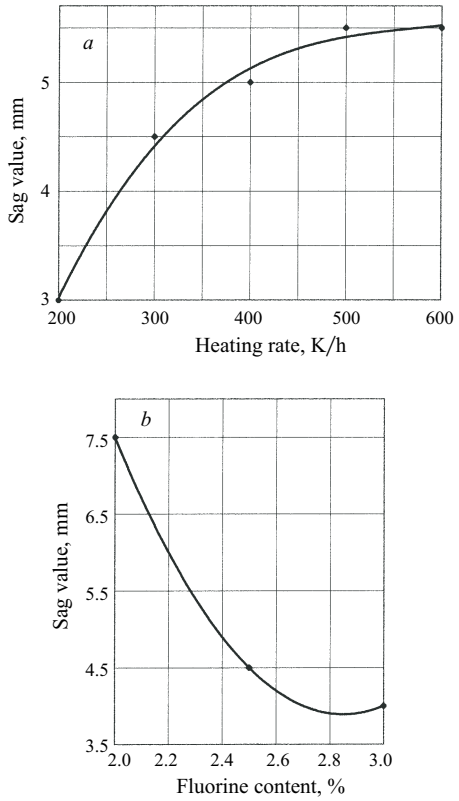

Fig. 1. The sample sag value versus the heating rate (*a*) and fluorine content in glass (*b*).

An example of the heat treatment regime developed for the production of glass ceramic material by continuous rolling is the treatment regime for slag glass ceramic [3]. The heat treatment is implemented in two steps; $t_1 = 650 – 750$°C, $\tau_1 = 15 – 30$ min; $t_2 = 850 – 950$°C, $\tau_2 = 15 – 45$ min; $v = 450 – 550$ K/h (t_1 and τ_1 are the temperature and the exposure duration in the first phase; t_2 and τ_2 are the same parameters in the second phase, v is the rate of the temperature rise from stage one to stage two). The overall heat treatment duration is around 1 h, with the speed of movement of the slag glass ceramic band equal to 55 – 70 m/h).

A two-stage procedure was proposed as well for the heat treatment of sygran plates produced by molding: $t_1 = 550 – 650$°C, $\tau_1 = 10 – 40$ min; $t_2 = 850 – 950$°C, $\tau_2 = 10 – 45$ min; $v = 200 – 400$ K/h, The total duration of the heat treatment is about 3 h. This procedure does not take into account the risk of vertical deformation, which can prevent using this regime for the continuous rolling method.

The present study investigated the effect of the technological parameters on the deformation of sygran produced by the rolling method. The variable parameters were the heat treatment conditions (t_2, τ_1, v), the fluorine content in the glass composition, and the geometrical dimensions of samples.

The quantitative value of deformation was determined by measuring the sag of the sample after heat treatment. The

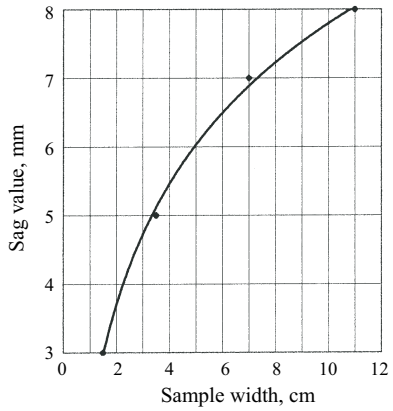

Fig. 2. Sag value versus the geometrical sizes of samples.

principal measurements were performed on samples cast in a rectangular mold 35 × 110 mm. The effect of the geometrical sizes of samples on deformation was studied using molds of width 35 – 110 mm and length 110 – 180 mm. The sample thickness remained constant: 15 mm. Immediately after molding, the samples were placed on supports in a muffle furnace and heat-treated in accordance with the prescribed regime. The distance between the supports varied from 70 to 125 mm.

The rate of the heating rise from the first to the second stage of heat treatment varied from 200 to 600 K/h. It was found that as the heating rate increases, the sag increases to a certain limit and then reaches a constant level (with $v > 450$ K/h) and does not grow any more (Fig. 1*a*). This is due to the fact that the heating rate becomes too high, and the required crystallization processes do not have time to take place inside the glass volume during the heating. In this case, the sag value is determined by the properties of the crystallized surface crust and the glass melt inside the sample volume.

The weight content of fluorine in samples varied from 2.0 to 3.5%. An increase in the fluorine content in glass decreases the sag (Fig. 1*b*). With an increasing fluorine content, crystallization is more intense, which increases the resistance of the material to deformation.

As for the geometrical sizes, as the sample width increases, the sag grows (Fig. 2). Taking into account this trend, one can expect a more significant sag of the sygran band in industrial conditions, since the band width will be larger.

It is known that the glass viscosity curve passes via a minimum during glass crystallization. With increasing temperature, the glass viscosity decreases until a certain temperature, above which the crystal phases start to emerge in the glass, and the viscosity of the glass-crystal system becomes higher. The minimum viscosity value determines the glass deformation limit, below which the article becomes deformed in the course of heat treatment.

The deformation limit of the glasses in the $CaO - SiO_2 - Al_2O_3$ system is $10^{7.5}$ Pa · sec [4]. This means that in the course of molding and heat treatment using the continuous rolling method, the viscosity should be at least $10^{7.5}$ Pa · sec. If this condition is satisfied, significant deformation of the band on the conveyor rollers can be avoided.

The typical relationships of viscosity and temperature for sygran and slag glass ceramics are shown in Fig. 3. It can be seen that both sygran and slag glass ceramic satisfy the above requirement: both dependence curves $\eta(t)$ pass via the minimum corresponding to $\log \eta \geq 7.5$ [Pa · sec]. This minimum for slag glass ceramics is within the temperature interval of 740 – 760°C. The probability of deformation is the highest within this interval. The temperature interval which is the most risky with respect to deformation for sygran is shifted to a higher temperature range, i.e. 850 – 880°C.

Knowing the viscosity value for a certain temperature, it is possible to estimate the glass sag value from the formula [5]:

$$\eta = 51.1 \frac{ml^3 z}{bh^3 f},$$

where η is the material viscosity, dPa · sec; m is the beam weight, g; l is the distance between the supports, cm; z is the time in which the sag increased, sec; b and h are the width and the height of the beam section, respectively, cm; f is the sag, cm.

The calculation results indicate that the theoretical sag of sygran samples in the temperature interval 860 – 950°C should not exceed 1 mm. According to the experimental data, the sag in heat-treated sygran samples exceeds the estimated values (Figs. 1, 2). At the same time, the sag in slag glass ceramic samples heat-treated under the same regime satisfied the estimated values, i.e., did not exceed 1 mm.

Thus, while the two materials contained equal quantities of the crystal phase, whose type and overall content were determined by x-ray phase analysis, the sag in sygran was greater than in slag glass ceramic and exceeded the estimated value. Consequently, sygran is less suitable for the rolling production method than slag glass ceramic.

This can be accounted for by the crystallization specifics of sygran. In the case of crystallization of slag glass ceramics, a fine-crystalline structure is formed throughout the entire glass volume. These crystals constitute the internal skeleton of the system and increase its resistance to deformation.

The crystallization of sygran proceeds in such a way that there is a small number of crystallization centers in the glass volume. The glass composition and the heat treatment procedure should provide for the formation of a small number of crystallization centers in the glass volume, which later grow into large spherulites. This is related to the structural specifics of sygran: the formation of a small quantity of sufficiently large spherulites (2 – 3 mm in diameter) is required for the formation of a macroheterogeneous structure. That is why the crystallization of sygran begins with the nucleation and growth of needle-shaped crystals on the band surface, which results in the formation of a crystalline crust.

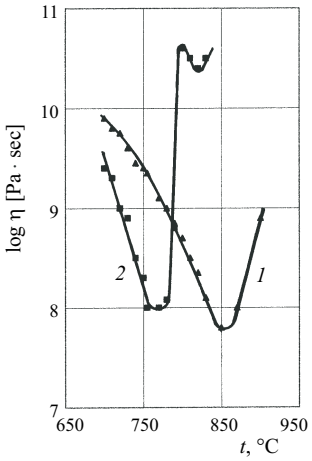

Fig. 3. Temperature dependence of viscosity in the interval of crystallization: *1*) white sygran; *2*) industrial white slag glass ceramic.

Thus, the needle-shaped crystals in sygran form a surface skeleton and not a volume skeleton, as in slag glass ceramics. The presence of the crystalline crust on the surface leads to increased viscosity, which was measured by the method of pressing an indenter into the sample surface (Fig. 3), whereas the viscosity inside the glass volume remains low. As the temperature increases, the viscosity of the glass volume decreases, making probable a substantial band deformation, which is registered in the case of sygran. This risk persists until the moment when the spherulites inside the glass band reach the size which enables them to agglomerate to each other and to the crystal crust. From this moment, the deformation resistance of the band becomes much higher. An increase in the number of spherulites in the band volume will make it possible to shorten the time needed to reach the elevated resistance to deformation.

Consequently, an increase in the exposure duration at the first stage of crystallization τ_1 can lead to higher deformation resistance, due to the increased number of crystallization centers and the number of spherulites formed.

In fact, as the time of exposure at the first stage of crystallization was increased by 15 min (from 15 to 30 min), less deformed samples were obtained. However, a further increase in τ_1 to 45 min did not lead to an improvement in the deformation properties.

An increase in the heating rate also affects the quantity of spherulites and their sizes. As the heating rate grows from 200 to 600 K/h, the spherulite size increases from 2.5 to 6.5 mm, whereas the number of spherulites per surface area unit decreases from 7.0 to 1.0 units/cm^2.

Thus, in order to reach the minimum band deformation value, the following recommendations should be observed:

– heat treatment should be performed in such a way that the sygran band stays at least 30 min within the temperature interval in which crystallization centers originate;

– the rate of the temperature rise from the first to the second stage should not be high, in order to avoid the deterioration of the crystalline structure and the deformation properties of the material;

– it is advisable to bring the starting temperature of crystallization nearer to the glass softening temperature by means of introducing at least 2.5 – 3.0 wt.% fluorine (or by means of modifying the glass composition);

– the exposure at the second stage of heat treatment should be carried out at a lower temperature than in the case of heat treatment of compressed plates.

It should be noted that in the production of glass ceramic materials using the continuous rolling method in industrial conditions, several limitations related to the structural specifics of the equipment are imposed on the above listed conditions.

Taking into account the specifics of sygran production by continuous rolling, we proposed the optimum heat treatment conditions, which make it possible to produce a glass ceramic material with the best structural and physicomechanical properties.

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